Producing Zirconium Diboride Components with Complex, Near-Net Shape Geometries by Aqueous Room-Temperature Injection Molding

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Advancing Ceramic Processing for Hypersonics

- Need for manufacturing complex-shaped ceramic components in aerospace
- Hypersonic flight speeds > Mach 5
  - Temperatures > 1900°C (3500°F)

NASA's X-43A hypersonic vehicle.

Image from www.nasa.gov/missions/research/x43
Wuchina, E., et al. *The Electrochemical Society Interface* (2007).

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Material	Melting Temperature (°C)	Density (g/cm^3)	Flexural Strength (MPa)	Elastic Modulus (GPa)
ZrB_2	3245	6.08	275-490	489-493
SiC	Dissociates 2245	3.21	480-580	410-444
Al_2O_3	2072	3.9	200-700	393
Stainless Steel AISI316L	1400	8	515-620	193
Aluminum 7075	900	2.8	228-572	71

Opeka, M.M., et al., *Journal of the European Ceramic Society, 1999.* ***19(13–14): p. 2405-2414.***
Fahrenholtz, W.G., et al., *Journal of the American Ceramic Society, 2007.* ***90(5): p. 1347-1364.***
Callister Jr., W. D., *Materials Science and Engineering An Introduction. John Wiley & Sons, Inc.: 2007; Vol. 7th.*

Advancing Ceramic Processing

- **Ceramic injection molding**
  - Net-shape production of parts possible
  - High-volume production
  - Pressureless sintering

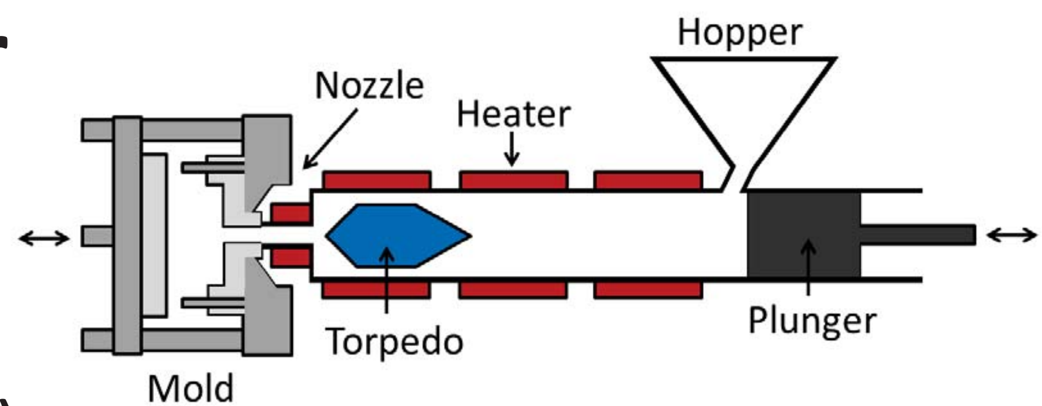
Parts fabricated by injection molding powders.

Image from http://www.aremco.com/wp-content.jpg

Previous Work on Ceramic Injection Molding

- **Ceramic injection molding**
  - Net-shape production of parts possible
  - High-volume production
  - Pressureless sintering

- **Polymer-based binder system in feedstock**
  - Thermoplastic polymer
  - Wax (carnauba, paraffin)
  - Plasticizer or dispersant



Schematic of conventional plunger-type injection molding apparatus.

German, R. M. and A. Bose, Injection Molding of Metals and Ceramics, Princeton, Metal Powder Industries Federation (1997).
Mutsuddy, B. C. and R. G. Ford, Ceramic Injection Molding, London, Chapman & Hall (1995).

Previous Work on Ceramic Injection Molding

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  - Net-shape production of parts possible
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- **Polymer-based binder system in feedstock**
  - Thermoplastic polymer
  - Wax (carnauba, paraffin)
  - Stearic acid

→**Energy-intensive heating and cooling of feedstock**

→**Non-aqueous, multi-component binders**

German, R. M. and A. Bose, Injection Molding of Metals and Ceramics, Princeton, Metal Powder Industries Federation (1997).
Mutsuddy, B. C. and R. G. Ford, Ceramic Injection Molding, London, Chapman & Hall (1995).

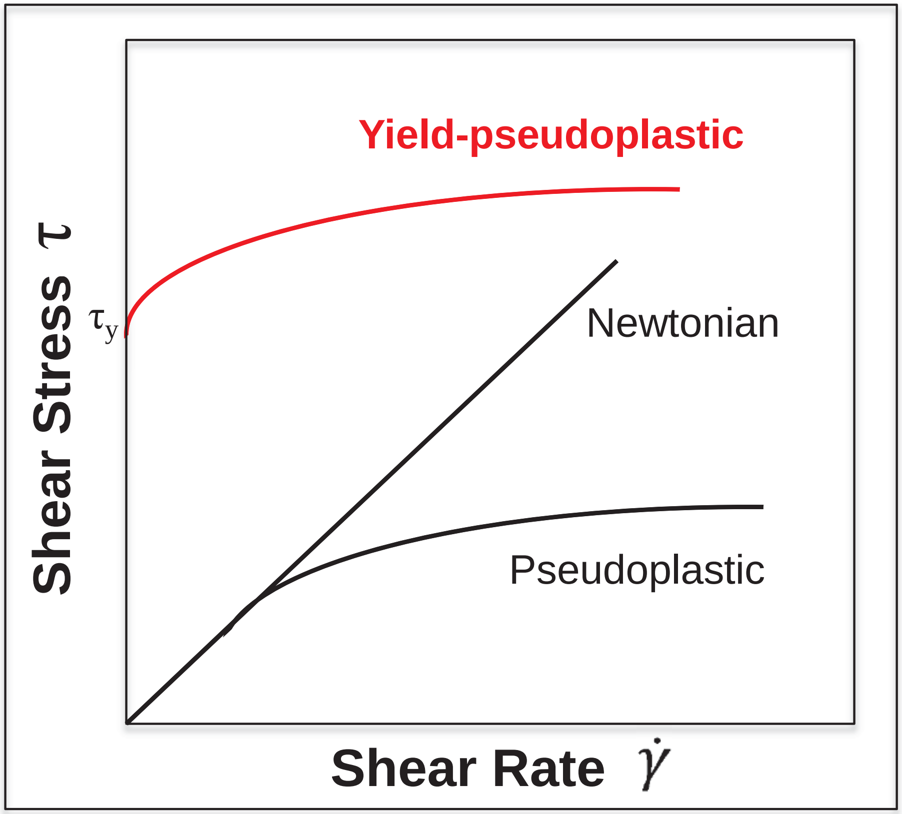
Ceramic Suspension Gel (CeraSGel)

- Suspension of ceramic powders in polymer gel
  - High ceramic content (~50 vol.%)
  - Minimal addition of water-soluble polymer (<5 vol.%)

Advantages

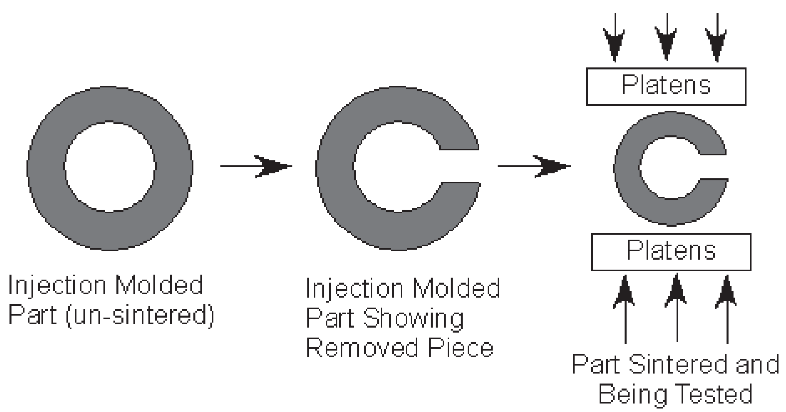
- Flowable at room temperature
- Yield-pseudoplastic
  - High yield point
  - Shear thinning

Sintered ZrB_2 specimen (right) formed by casting CeraSGels.

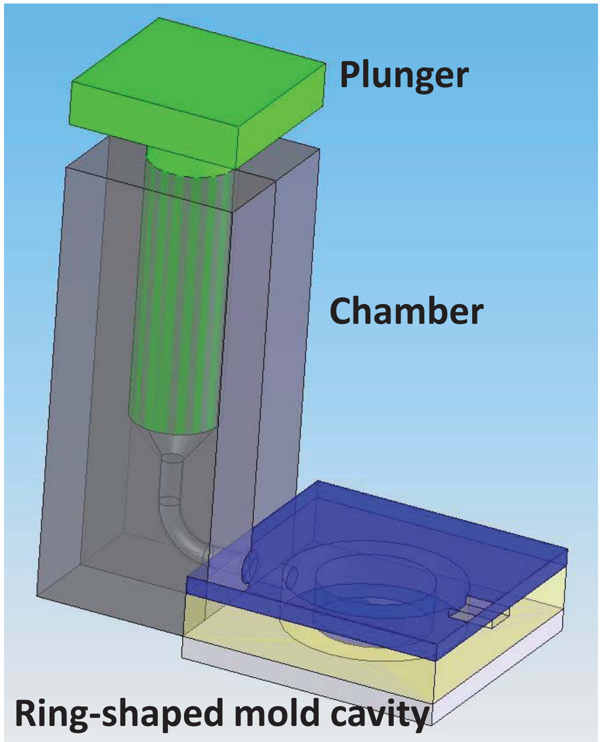


Injection Mold Design and Setup

- Force at constant rate exerted onto plunger to force CeraSGel out of chamber into mold
  - MTS setup
- Mold design
  - Mechanical characterization using ASTM C1323-10



  - Machine C-shape from ring



Schematic of injection mold device.

ASTM C 1323-10, “Standard Test Method for Ultimate Strength of Advanced Ceramics with Diametrally Compressed C-Ring Specimens at Ambient Temperature,” (2010).

CeraSGel Injection Molding Process

Mix powder + H_2O + dispersant and ball mill

Mix water + PVP by magnetic stirring

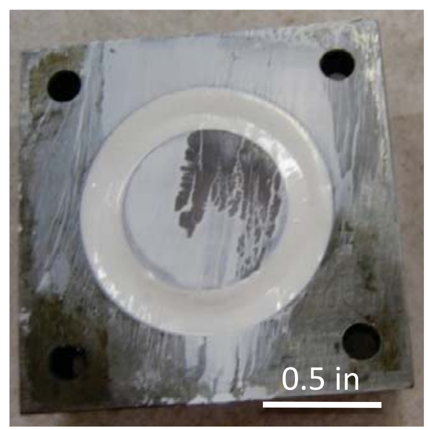
Add water-PVP mixture to ceramic slurry, ball mill

Alumina CeraSGel

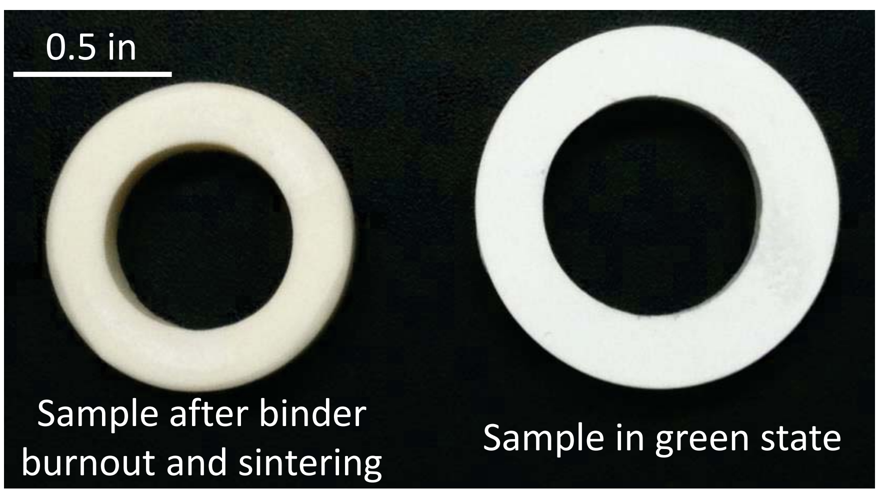
Load CeraSGel into mold chamber using syringe

Place mold between MTS platens, apply force at constant rate

Remove sample from mold, air dry



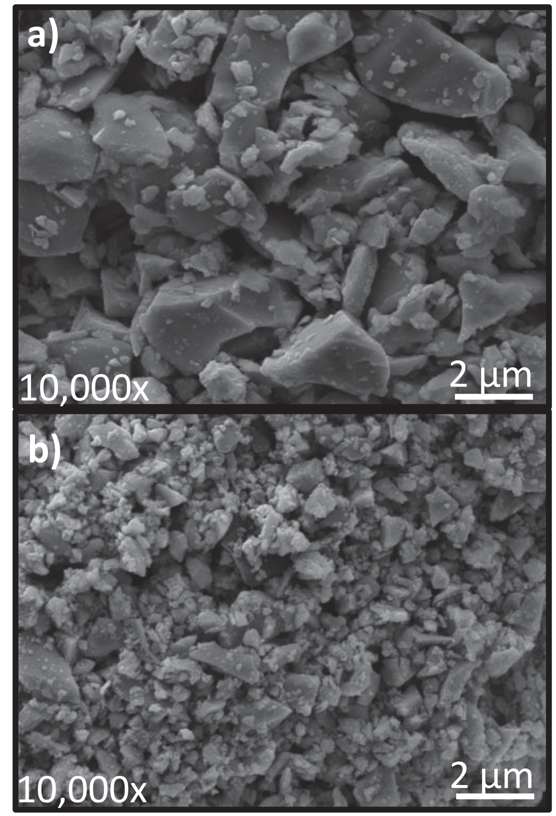
Burnout binder and pressureless sinter part to obtain a part near full density



Wiesner, V.L., J.P. Youngblood, and R.W. Trice, *Journal of the European Ceramic Society, 2014.* ***34(2): p. 453-463.***

ZrB_2 CeraSGel Material Selection

- *Pressureless sintering* of ZrB_2 typically >2000°C
  - ZrB_2 sensitive to oxygen impurities
  - B_4C sintering aid
  - Attrition mill using WC media
- Dispersant to maximize ZrB_2 powder loading
- PVP as binder to tailor flow properties



SEM images of a) as-received ZrB_2 powders (H.C. Starck Grade B); b) ZrB_2+B_4C powders after attrition milling with WC media resulting in d_{50}~0.5 µm.

Zhang, S.C., G.E. Hilmas, and W.G. Fahrenholtz, *Journal of the American Ceramic Society, 2006.* ***89(5): p. 1544-1550.***
Fahrenholtz, W.G., et al., *Journal of the American Ceramic Society, 2008.* ***91(5): p. 1398-1404.***

Characterizing CeraSGel Formulations

Evaluate effect of PVP content in CeraSGels containing 48.6 vol.% ZrB_2+B_4C+WC

- 1 vol.% PVP
- 2 vol.% PVP
- 3 vol.% PVP

- Rheological behavior of CeraSGels
- Machinability in green state
- Density and composition after binder removal and pressureless sintering
- Mechanical strength of sintered samples

Rheological Dependence on Polymer Content

Vary PVP amount in CeraSGel

- 1 vol.% PVP
- 2 vol.% PVP
- 3 vol.% PVP

Polymer Content	pH	Estimated Yield Stress [Pa]
1 vol.%	8.85 ± 0.1	**567**
2 vol.%	8.91 ± 0.1	**405**
3 vol.%	8.89 ± 0.1	**235**

– pH of suspensions constant for PVP contents

→PVP content does not alter pH

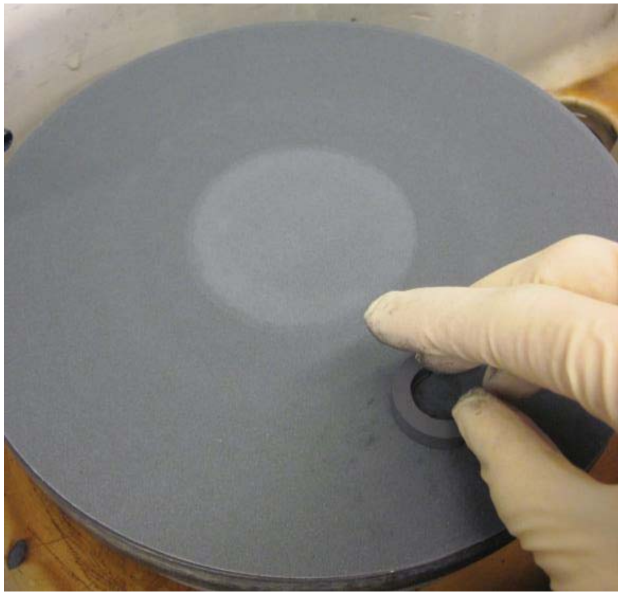
– Time-dependent response

– Use creep test approach to approximate yield shear stress for ZrB_2+B_4C+WC suspensions

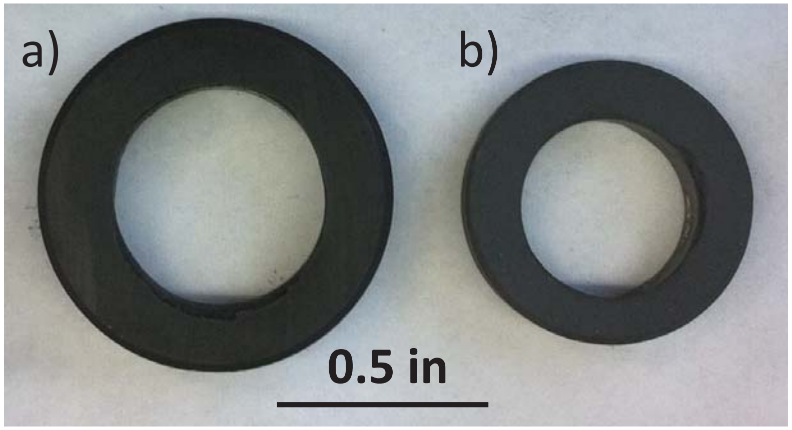
→Yield stress decreases with increasing polymer content

Machinable in Green State

- Prepare sample in green state
  - Even out surfaces by polishing
  - Chamfer edges
- **Binder burnout and pressureless sintering**
  - Ramp to 600°C (4°C/min), 1h hold (vacuum)
  - 1650°C (10°C/min), 1h hold, begin argon backfill
  - 1850 (10°C/min), 1.5h hold in argon



Preparing green body for mechanical testing.



a) ZrB_2 sample in green state and b) after binder burnout and sintering.

Zhang, S. C., et al., *Journal of the American Ceramic Society*, **89**(5): 1544-1550 (2006).
He, R., et al., *Ceramics International*, **38**(7): 5411-5418 (2012).

PVP Effect on Density and Internal Porosity

- **Archimedes density test**
  - True density (TD) = 6.17 g/cm^3
    - Based on 86 wt.% ZrB_2, 4 wt.% B_4C and10 wt.% WC

PVP content	Relative density (TD%)
1 vol.%	99.4 ± 0.3
2 vol.%	100.5 ± 0.4
3 vol.%	98.2 ± 0.8

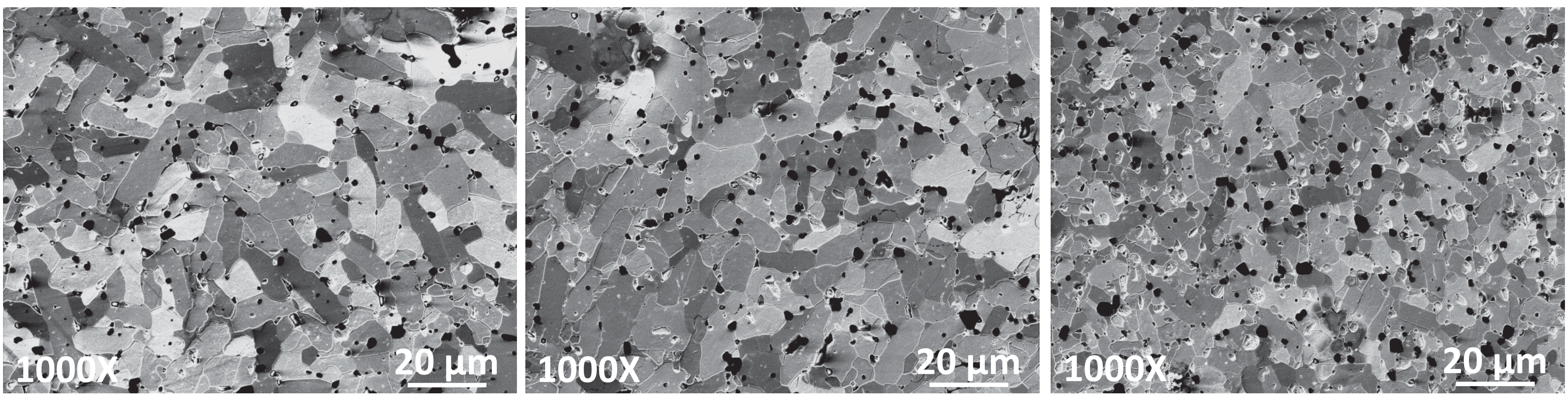
  - Specimens prepared with 3 vol.% PVP had lowest density
  - ~21% linear shrinkage

PVP Effect on Density and Internal Porosity

Scanning electron microscopy (SEM)

- Dense microstructure
- Grain size dependence

PVP content	Relative density (TD%)	Average grain size (µm)
1 vol.%	99.4 ± 0.3	9.8 ± 6.2
2 vol.%	100.5 ± 0.4	10.6 ± 5.3
3 vol.%	98.2 ± 0.8	7.7 ± 3.7



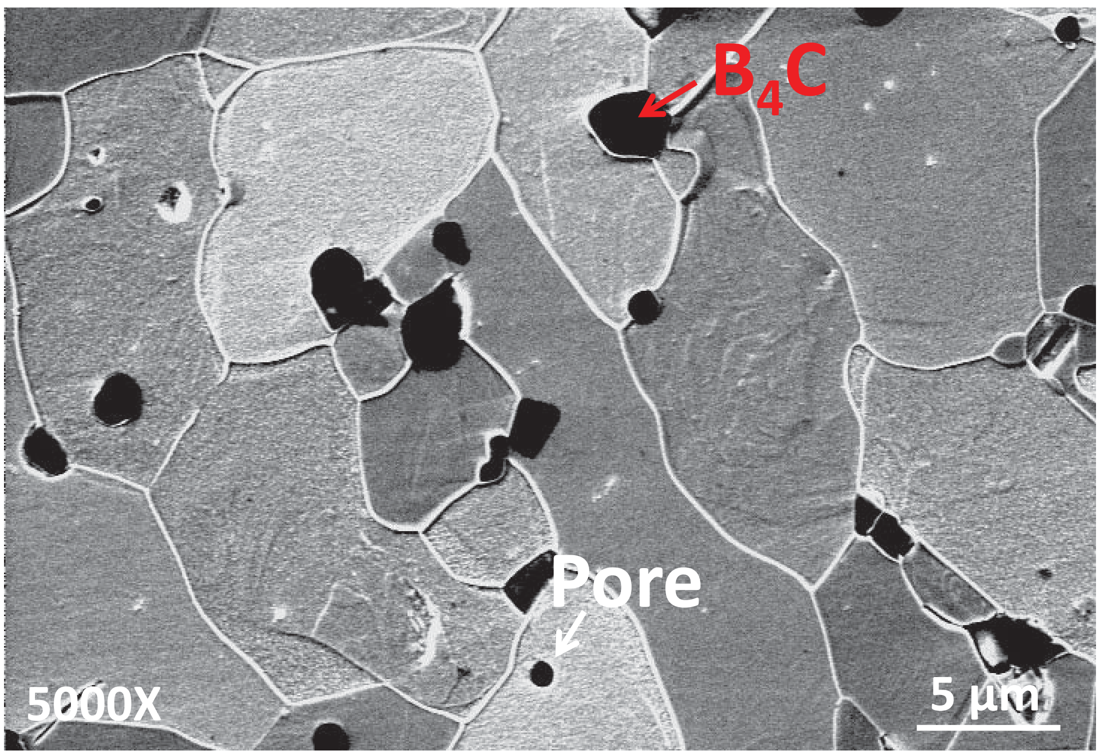
1 vol.% PVP 2 vol.% PVP 3 vol.% PVP

→Unclear if polymer content affects grain size of sintered part

Elemental Analysis of Sintered Specimens

Energy dispersive spectroscopy (EDS)

- B_4C grains surrounded by ZrB_2 grains
- No presence of oxygen detected



Cross section of specimen prepared with 1 vol.% PVP CeraSGel.

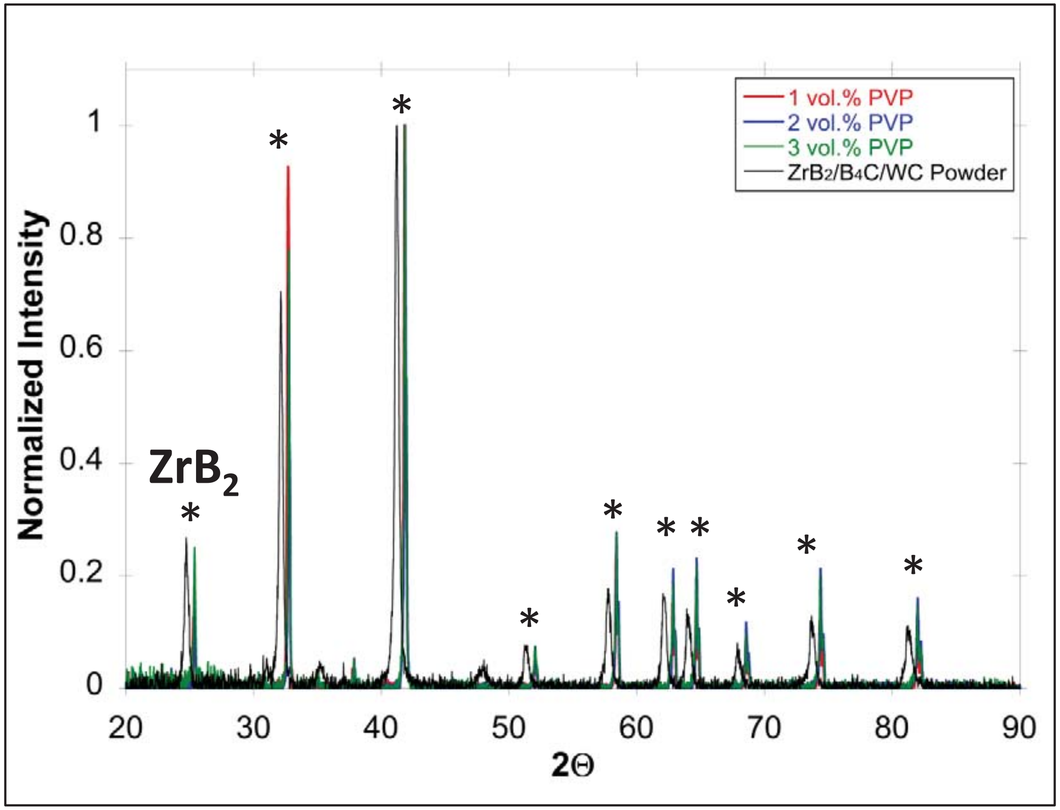
Phase Analysis of Sintered Specimens

- Tungsten formed solid solution with ZrB_2

  →ZrB_2 peaks shifted to higher angles after sintering

- No oxide phases detected

✓**Binder content did not seem to affect sintered ceramic compositions**



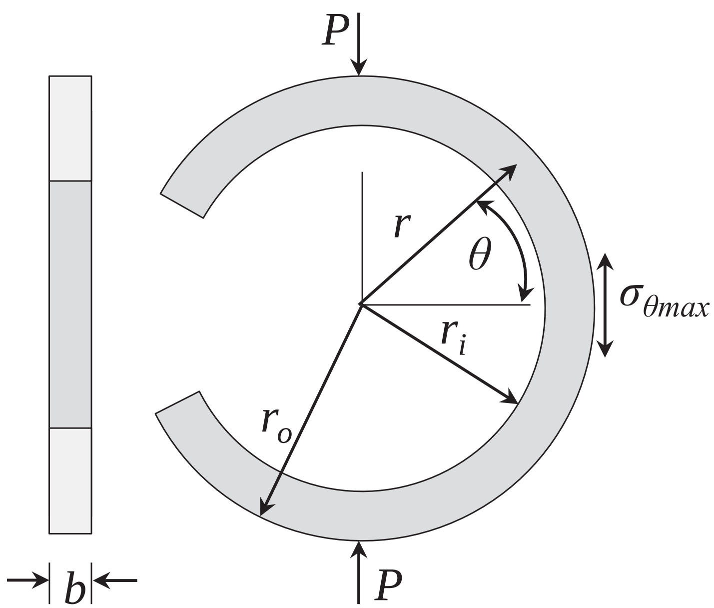
XRD spectra of sintered ZrB_2 specimens prepared with 1, 2 and 3 vol.% PVP CeraSGels and of attrition milled $ZrB_2/B_4C/WC$ powders.

Mechanical Strength of Sintered Parts

ASTM C 1323-10[1]

Ultimate strength at ambient temperatures

- Requires compressive loading of C-ring specimens



Geometry of C-ring specimen for ASTM C 1323-10 (modified from standard[1]).

$$\boxed{\sigma_{\theta\,\max} = \frac{PR}{btr}\left[\frac{r_o - r_a}{r_a - R}\right]}$$

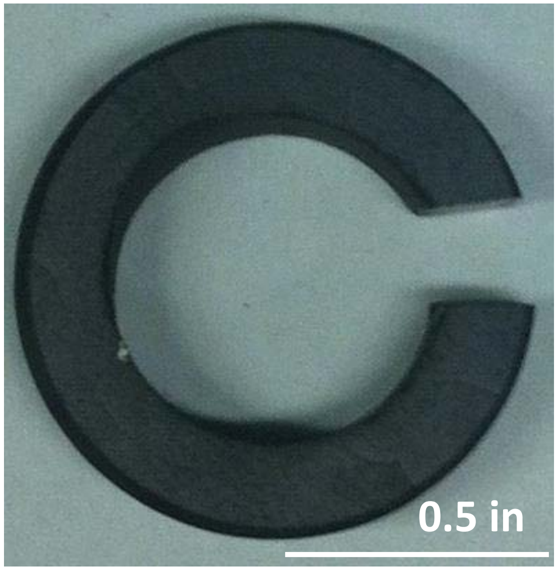
$$R = \frac{(r_o - r_i)}{\ln(r_o / r_i)} \qquad r_a = \frac{r_o + r_i}{2}$$

ASTM C 1323-10, "Standard Test Method for Ultimate Strength of Advanced Ceramics with Diametrally Compressed C-Ring Specimens at Ambient Temperature," (2010).

Effect of PVP on Average C-ring Strength of ZrB_2 Samples

- C-ring strength values lower than anticipated
  - ASTM C 1323-10 not comparable to other flexure tests
- Grain sizes comparable to literature
- Defects introduced during forming

PVP Content in vol.% (wt.%)	Relative density (TD%)	Average C-ring strength (MPa)
1 (0.3)	99.4 ± 0.3	**31 ± 12**
2 (0.7)	100.5 ± 0.4	**73 ± 15**
3 (1.0)	98.2 ± 0.8	**75 ± 27**

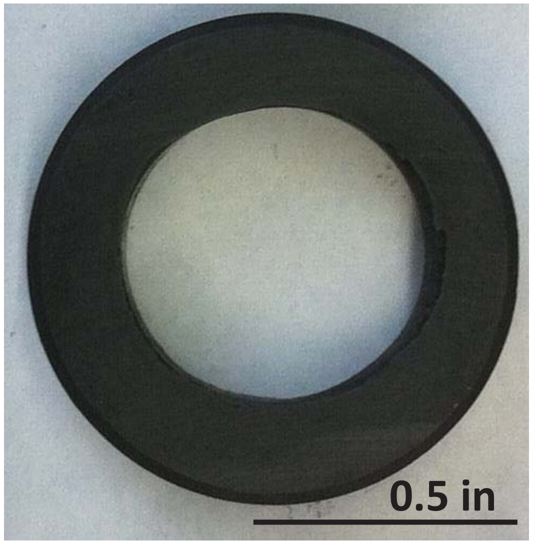


Final sintered C-shaped sample.

→ Evaluate ZrB_2-based CeraSGels with varying PVP contents and powder loadings

Conclusions and Future Work

- **Rheology of ZrB_2+B_4C+WC CeraSGels**
  - Flow properties suitable for room-temperature processing
  - Effective yield point decreased with increasing PVP content
- **Machinable in green state**
- **Dense (>98%TD) ZrB_2 samples produced by pressureless sintering**
  - 21% linear shrinkage
  - PVP did not affect final composition
- **Mechanical characterization using ASTM C 1323-10**
  - C-strength increased with increasing PVP content



Dense ZrB_2 rings have been fabricated by room-temperature injection molding of CeraSGels.

→Prepare and evaluate CeraSGels and resulting C-ring specimens containing >3 vol.% PVP with varying solids loading